

Cross-linked sulfonated poly(phthalazinone ether ketone)s for PEM fuel cell application as proton-exchange membrane

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Abstract

The cross-linkable sulfonated poly(arylene ether)s derived from 3,3'-diallyl-4,4'-dihydroxybiphenyl, bisphthalazinone, 4,4'-difluorobenzophenone (DFBP) and sulfonated 4,4'-difluorobenzophenone (SDFBP) were synthesized over a wide range of DFBP/SDFBP molar ratios. The resulting sulfonated poly(arylene ether)s with high inherent viscosity ($1.02\text{--}1.29\text{ dL g}^{-1}$) are soluble in polar organic solvents and can form flexible and transparent membranes by casting from their solution. Cross-linking reaction was carried out using the thermal activated radical cross-linking agent (TARC) at $140\text{ }^{\circ}\text{C}$. The comprehensive properties of the virgin and the cross-linked membranes were compared accordingly. The results showed that the cross-linked membranes revealed the better mechanical, oxidative and dimensional stabilities together with high proton conductivity ($9.675 \times 10^{-3}\text{ S cm}^{-1}$) at $25\text{ }^{\circ}\text{C}$ under 100% relative humidity.

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Keywords: Cross-linking; Proton conductivity; Sulfonation; Membrane

1. Introduction

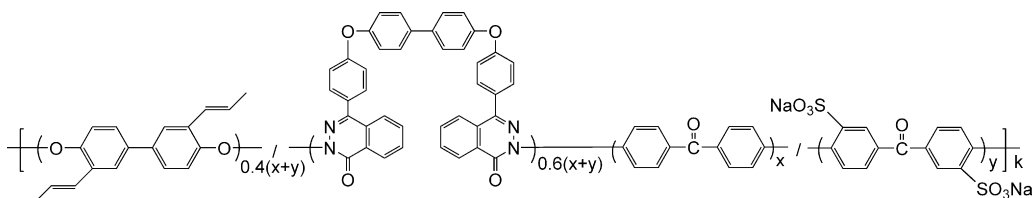
Recently, the emergence of the proton-exchange membrane fuel cell (PEMFC) has promoted the development of novel cation-exchange materials. The proton-exchange membranes for PEM fuel cell must show following property profile: (i) highly chemical, thermal and mechanical stabilities in harsh environment; (ii) as low as possible water uptake connected with high proton conductivity [1,2]. Nafion perfluorinated resins that contain perfluorosulfonic acid groups have outstanding properties as membranes in polymer electrolyte membrane fuel cells when used up to about $80\text{ }^{\circ}\text{C}$. However, perfluorinated polymers are expensive, have relatively poor resistance to methanol transport, which is important in direct methanol fuel cells (DMFC), and at the higher temperatures dehydration of the membrane occurs with concomitant loss of conductivity [3].

The need for alternatives to copolymers containing perfluorosulfonic acid groups has led to the development of

a number of aromatic sulfonated polymers as membrane candidates [4–16]. Poly(ary ether)s (PAE)s are high performance polymers that possess good mechanical properties and excellent thermal, oxidative, and chemical stability, and therefore they have been extensively studied as a base for new ionomeric materials [17,18]. Much effort has devoted to develop sulfonated PAEs by direct polymerization, of which the sulfonic acid groups are attached onto the deactivated aromatic rings [19,20]. These sulfonated aromatic polymer membranes require a high sulfonation level to achieve sufficient proton conductivity. Unfortunately, such a high sulfonation level makes them excessively water-swollen or soluble in water. In this case, highly sulfonated polymer membranes lose their mechanical properties and become unavailable in PEMFC applications.

Cross-linking could be a simple and powerful solution to control such indispensable properties including high proton conductivity, excellent mechanical properties, and good dimensional stability. So far, there have been several studies on the cross-linking of sulfonated polymer membranes. The covalently cross-linking of sulfonated poly(ether ether ketone) (PEEK) via a thermally activated reaction of polyatomic alcohols and sulfonic acid groups [21,22], covalently cross-linking of the

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Scheme 1. The structure of sulfonated poly(phthalazinone ether ketone)s.

polymer consisting of sulfinate and sulfonate groups by a thermally activated reaction of 1,4-diiodobutane and sulfinate groups [23]. However, these methods are based on the crossing mechanism involving elimination of sulfuric acid, resulting in the increased cross-linking density invites and reduced proton conductivity. For the ionic cross-linking of acid–base blend membranes [24,25], since this method requires for incorporating basic polymer having neither water solubility nor high water absorption, the resulting polymer shows low content of protonic acid group and the low proton conductivity.

In previous works, we found that bisphthalazinone monomers can readily react with activated dihalides to give high molecular weight PAEs via a N–C coupling reaction [26–29]. To produce a polymer electrolyte to meet the requirements for PEM fuel cells, we have designed aromatic copolymers containing sulfonated benzophenone, benzophenone, biphtalazinone and propenyl moieties (Scheme 1). The propenyl attached onto the backbone functions as cross-linkable group.

The cross-linked PAE is to exhibit excellent proton conductivity, long durability and low water uptake.

2. Experimental

2.1. Materials

2-(4-Chlorophenyl) benzoic acid (Taixin SUUMY Fine Chemical Co., Ltd., Jiang Su China) was recrystallized from ethanol. 4,4'-Dihydroxyphenyl, allylbromide and 4,4'-difluorobenzophenone **4** (DFBP) were purchased from Aldrich Chemical Co. and used as received. Sulfonated 4,4'-difluorobenzophenone **5** (SDFBP) were synthesized as outlined in Ref. [30]. Reagent-grade hydrazine monohydrate, methanol, *N,N'*-dimethylacetamide (DAMc), dimethyl sulfoxide (DMSO), toluene, methanol, and anhydrous potassium carbonate were obtained from commercial sources and used without further purification. DMSO was dried over 4 Å molecule sieves and toluene was dried over sodium wire prior to use.

2.2. Instrumentation

The ^1H NMR spectra were recorded on a Bruker NMR instrument (model DRX 400 MHz); chemical shifts were given in ppm against tetramethylsilane as an internal standard. Elemental analyses were performed on an Elementar elemental analyzer (model Varios EL). Melting points were taken on a XT4A melting point apparatus. Inherent viscosity was determined for a solution of 0.5 g dL^{-1} in DMAc at $30\text{ }^\circ\text{C}$ with a calibrated Ubbelohde viscometer.

3. Membrane characterization

3.1. Ion exchange capacity (IEC)

The IEC of the membranes were determined by titration according to the literature [31]. A dry weight of 0.5–1.0 g of the polymer membrane in the acid form was immersed into saturated NaCl solution to replace the protons of sulfonic acid groups with sodium ions. The replaced protons were titrated using 0.1 M NaOH solution, with phenolphthalein as indicator. The moles of the proton are equal to the moles of sulfonic group and the IEC was calculated from the titration data using the following equation:

$$\text{IEC (mol g}^{-1}\text{)} = \frac{\Delta V_{\text{NaOH}} C_{\text{NaOH}}}{W_s} \quad (1)$$

where ΔV_{NaOH} is the consumed volume of NaOH solution, C_{NaOH} the concentration of NaOH solution and W_s is the weight of the membrane sample.

3.2. Water uptake and swelling ratio [32,33]

The membrane was dried under vacuum at $80\text{ }^\circ\text{C}$ for 24 h. The weighed membrane was immersed in deionized water at $80\text{ }^\circ\text{C}$ for 24 h. Wet membrane was weighed quickly upon wiping up its surface water with tissue paper. The water uptake of membrane was calculated according to the following equation:

$$\text{water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (2)$$

where W_{wet} and W_{dry} are wet and dried membrane weights, respectively.

The dimensional stability of the membrane was characterized by the swelling ratio and the volume swell.

The swelling ratio was calculated from the following equation:

$$\text{swelling ratio (\%)} = \frac{L_w - L_d}{L_d} \times 100 \quad (3)$$

where L_w and L_d are the lengths of the cross of the wet membrane and dry membrane (test area $1\text{ cm} \times 2\text{ cm}$), respectively.

The volume swell was calculated from the following equation:

$$\text{volume swell (\%)} = \frac{\Delta V}{V} \times 100 \quad (4)$$

where $\Delta V = V_{\text{wet}} - V_{\text{dry}}$, $V = \text{length} \times \text{width} \times \text{thickness}$, the length, width and thickness of the test samples were 2 cm, 1 cm and 100–130 μm , respectively.

3.3. Proton conductivity

Proton conductivity measurement was performed on fully hydrated film samples at temperature 25 °C at 100% relative humidity with a Solartron 1255B frequency response analyzer at an oscillating voltage of 10 mV, using a two probe method at frequency ranging from 1 MHz to 5 KHz. The cell assembly was similar to that used in the literatures [34,35]. The proton conductivity (σ) of the specimen in the transverse direction (across the membrane) was calculated from the impedance data according to the following equation:

$$\sigma = \frac{d}{RS} \quad (5)$$

where d and S are the thickness and the face area of the specimen, respectively, and R is derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the $\text{Re}(Z')$ -axis.

3.4. Oxidative and hydrolytical stability

Oxidative stabilities were determined using Fenton's reagent (3 wt% H_2O_2 + 2 ppm FeSO_4) at 80 °C. The membranes were immersed in Erlenmeyer flask containing Fenton's reagent. The flask was shaken vigorously once every 10 min until the membrane began to break. The hydrolytic stability was also investigated by treating membrane samples in boiling water for more than 100 h. There was not any change observed in both the membrane's shape and appearance, implying that no hydrolysis occurred during the treatment.

3.5. Thermal stability

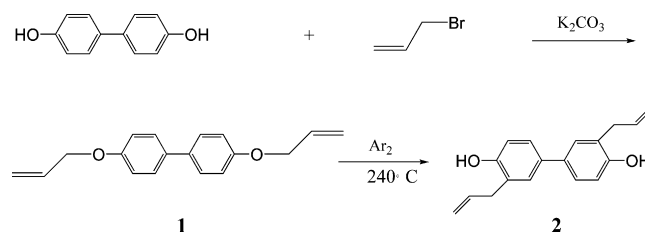
The thermal stability of the sulfonated PAEs was determined with a Seiko SSC-5200 thermal gravimetric analyzer under a nitrogen atmosphere (200 mL min^{-1}) at temperature range of 70–600 °C. The heating rate was $20 \text{ }^\circ\text{C min}^{-1}$.

3.6. Mechanical properties

The tensile properties were determined at 25 °C and 50% relative humidity by SANS (Shenzhen, China) electromechanical universal test machine (model CMT-4014). The samples were cut into a size of 5 mm \times 50 mm. The cross-head speed was set at a constant speed of 10 mm min^{-1} . For each testing reported, at least three measurements were taken and average value was calculated.

3.7. Gel content

The gel content of the cross-linked samples was determined according to ASTM D2765 method using a Soxhlet extractor, DMAc was used as solvent. Samples were refluxed in DMAc for at least 48 h, until the sample attained a constant weight. The residue after extraction was taken as the gel component, and the



Scheme 2. Synthesis of monomer **2**, 3,3'-diallyl-4,4'-dihydroxybiphenyl.

gel content was calculated according to the following equation:

$$\text{gel content (\%)} = \frac{W_2}{W_1} \times 100 \quad (6)$$

3.8. Preparation of 3,3'-diallyl-4,4'-dihydroxybiphenyl **2** [36]

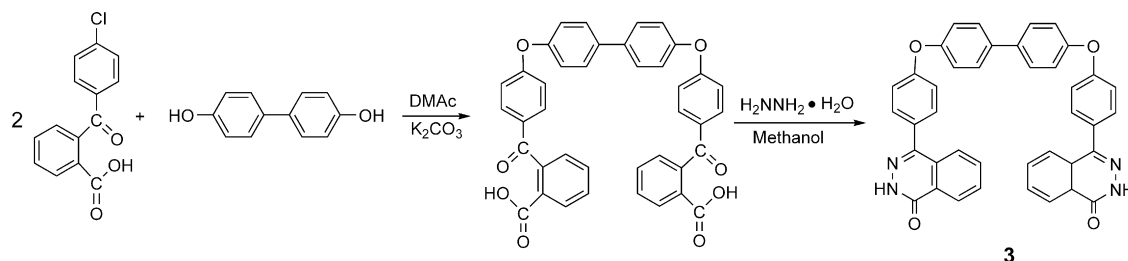
To a 50 mL three-necked round-bottom flask equipped with a Dean-stark trap, a condenser, nitrogen inlet/outlet and a magnetic stirrer, 4,4'-dihydroxybiphenyl (9.31 g, 50 mmol), anhydrous K_2CO_3 (7.60 g, 55 mmol), DMAc (20 mL), and toluene (20 mL) were charged. The reaction is depicted as Scheme 2. Nitrogen was purged through the reaction mixture with stirring for 15 min, and then the mixture was heated to 150 °C and kept at this temperature for 3 h. After the produced water was azeotroped off with toluene, the temperature was cooled to 110 °C and the Dean-stark trap was removed. 7.26 g allylbromide (60 mmol) was added to the reaction mixtures. After 8 h, water was added and the crystalline powders were collected, washed for several times with boiling 95% ethanol, finally filtered and dried in oven to give **1** (mp 154 °C, yield 92%). Following the Claisen rearrangement procedure, the compound **1** was kept at 240 °C under argon for 30 min, upon cooling to room temperature, the precipitates were filtered off and recrystallized in boiling heptane to obtain **2** (yield 76%); mp: 82–83 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 3.45 (d, 4H), 4.99 (s, 2H), 5.13–5.25 (m, 4H), 5.97–6.14 (m, 2H), 6.87 (d, 2H), 7.27–7.30 (q, 2H), 7.30–7.31 (d, 2H). Elem. Anal. for ($\text{C}_{18}\text{H}_{18}\text{O}_2$) (266.33): Calcd.: C, 81.17%; H, 6.81%. Found: C, 80.94%, H, 6.84%.

3.9. Preparation of bisphthalazinone **3** biphenyl moiety containing

Bisphthalazinone monomer **3** was synthesized as reported in Ref. [27] in a two-step sequence as depicted in Scheme 3. The nucleophilic substitution reaction of 2-(4-chlorophenyl) benzoic acid with 4,4'-dihydroxybiphenyl gave dicarboxylic acid, which was converted to bisphthalazinone **3** by refluxed with hydrazine monohydrate in methanol via the ring-closure reaction (yield 91%). mp: 358–360.

$^1\text{H NMR}$ (400 MHz, $\text{DMSO}-d_6$) δ (ppm): 7.20–7.23 (m, 8H), 7.63 (d, 4H), 7.73–7.75 (m, 6H), 7.88–7.92 (m, 4H), 8.33 (m, 2H), 12.85 (s, 2H).



Scheme 3. Preparation of bisphthalazone 3.

3.10. Preparation of sulfonated poly(phthalazinone ether ketone)s **6a–e**

The typical procedure for the synthesis of SPAEs **6a–e** is as follows (Scheme 4): to a 25 mL three-neck flask equipped with a Dean-Stark trap, an nitrogen inlet/outlet, a condenser, and a magnetic stirrer was added previously synthesized monomer **2**, 3,3'-diallyl-4,4'-dihydroxybiphenyl (0.213 g, 0.8 mmol), monomer **3**, bisphthalazinone (0.752 g, 1.2 mmol), the mixture of monomer **4**, 4,4'-difluorobenzophenone and monomer **5**, sulfonated 4,4'-difluorobenzophenone (2 mmol), anhydrous potassium carbonate (3.50 g, 2.5 mmol), 8 mL of DMSO and 9 mL of toluene. The mixture was refluxed for 3 h at 140 °C to azeotrope off the formed water with toluene. After distilling off the excess toluene, the temperature was slowly raised to 170 °C and maintained at this temperature for 15 h. Before cooling down the reaction mixture 5 mL DMSO was added to dilute the reaction solution. The result viscous polymer solution was poured into the mixture of methanol/water (1:1, v/v) to precipitate out the polymer. The precipitates were filtered off and washed with water. The recovered polymers were dried at 110 °C under vacuum for 24 h.

3.11. Preparation of the membranes from **6a–e** and **6a^c–e^c**

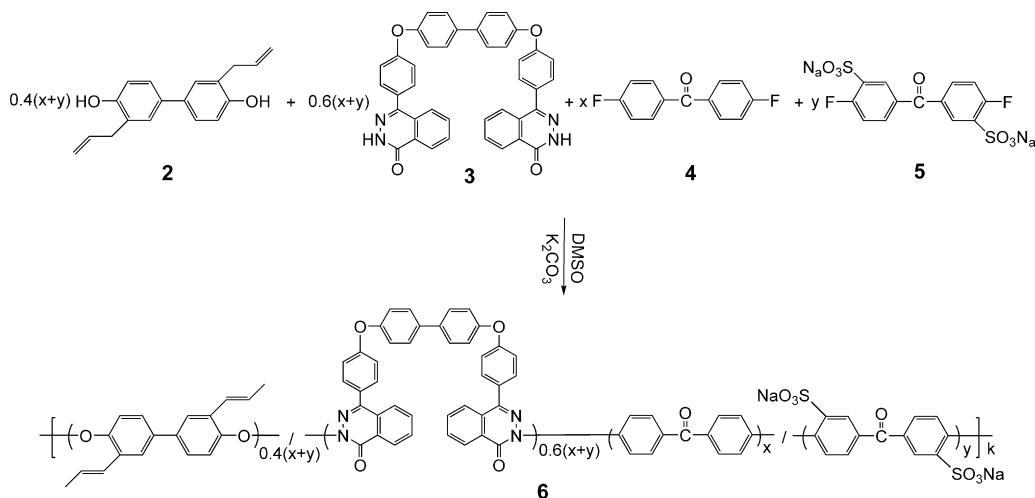
Membranes of the SPAEs **6a–e** (sodium salt form) were prepared by casting their 5% solutions in DMAc on a glass plate

and dried at 60 °C for 12 h and then at 80 °C under vacuum for 2 days. Membranes of cross-linked polymers **6a^c–e^c** (sodium salt form) were prepared by casting their 10% solutions in DMAc with DCP as thermal activator or initiator, then annealing at 140 °C under nitrogen protection [37].

4. Results and discussion

4.1. Synthesis of SPAEs **6a–e**

The N–H group of the phthalazinone has been proved to behave like phenolic O–H groups [38]. Similarly, the monomer **3** bisphthalazinone with two phthalazinone groups should react like bisphenols in nucleophilic aromatic substitution reactions via a novel N–C coupling reaction. The SPAEs **6a–e** with different sulfonation degree were prepared from aromatic nucleophilic polycondensation of **2** (0.8 mmol) and **3** (1.2 mmol) with various content of DFBP **4** and SDFBP **5** (Scheme 4). The resulting polymers are all soluble in polar organic solvents, such as DMSO, DMF, DMAc and NMP. The cross-linking density can then be readily controlled by adjusting the ratio of monomer **2** to monomer **3**, while the sulfonation degree can be altered by changing the ratio of monomer **4** to monomer **5**. In this sense, the desired properties such as the proton conductivity, the water uptake and the mechanical strength of the synthesized SPAE **6** can be achieved accordingly.



Scheme 4. Preparation of sulfonated poly(phthalazinone ether ketone)s.

Table 1
The polymerization results of sulfonated poly(phthalazinone ether ketone)s

Polymer	Monomer 4 (mmol)	Monomer 5 (mmol)	$[\eta]^a$ (dL g ⁻¹)	Yield (%)	IEC ^b ($\times 10^{-3}$ mol g ⁻¹)	IEC ^c ($\times 10^{-3}$ mol g ⁻¹)
6a	1.6	0.4	1.2	96	0.57	0.49
6b	1.2	0.8	1.25	97	1.08	0.93
6c	0.8	1.2	1.06	93	1.54	1.46
6d	0.4	1.6	1.38	93	1.87	1.82
6e	0	2.0	1.02	95	2.32	2.27
Nafion 117	–	–	–	–	0.91 ^d	0.83

^a Tested in 0.5 g dL⁻¹ solution in DMAc at 30 °C.

^b Calculated IEC of the SPAEs.

^c Measured IEC of the SPAEs.

^d Ref. [40].

4.2. Preparation of the membranes from **6a–e** and **6a^c–e^c**

Membranes of the SPAEs **6a–e** (sodium salt form) were prepared by casting their 5% solutions in DMAc on a glass plate and dried at 60 °C for 12 h and then at 80 °C under vacuum for 2 days. Membranes of cross-linked polymers **6a^c–e^c** (sodium salt form) were prepared by casting their 10% solutions in DMAc with DCP as thermal activator or initiator, then annealing at 140 °C under nitrogen protection. By this process, the flexible, ductile, and transparent membranes can be obtained. All the cross-linked polymers were tested to be not soluble in polar organic solvents and the gel contents of the cross-linked polymers **6a^c–e^c** are listed in Table 2. The results proved that the propenyl groups of the virgin polymers had been cross-linked. The gel content decreased with increasing the sulfonation degree of these SPAEs. This implies that the sulfonated groups had influence on the cross-linking reaction. Presumably, this resulted from the less solubility of DCP in the polymer solution.

The membranes (in sodium salt form) were transformed to proton form by soaking in deionized water for 1 day at room tem-

perature, and then by immersion in 2.0N HCl solution for 24 h. The obtained acid form membranes were washed by immersion in deionized water for 24 h, during this process the water was changed for at least three times. The thickness of all membrane samples were controlled in the range of 100–130 μm when cast.

4.3. Properties of SPAEs **6a–e** and cross-linked SPAEs **6a^c–e^c**

The polymerization results of SPAEs **6a–e** are listed in Table 1. The inherent viscosity of the synthesized polymers ranged from 1.02 to 1.38 dL g⁻¹, demonstrating very high molecular weight of the resulting polymers in high yield of $\geq 93\%$. The IEC of the sulfonated SPAEs determined by titrating was in good agreement with the expected values within the experimental deviation. This implies that the pendant sulfonic acid groups were quantitatively attached to the polymer chains. It can be seen from Table 1 that the SPAEs **6b–e** had higher IEC than the Nafion 117. The ¹H NMR spectrum of polymer **6c** is shown in Fig. 1. Comparing ¹H NMR data of monomer **2**

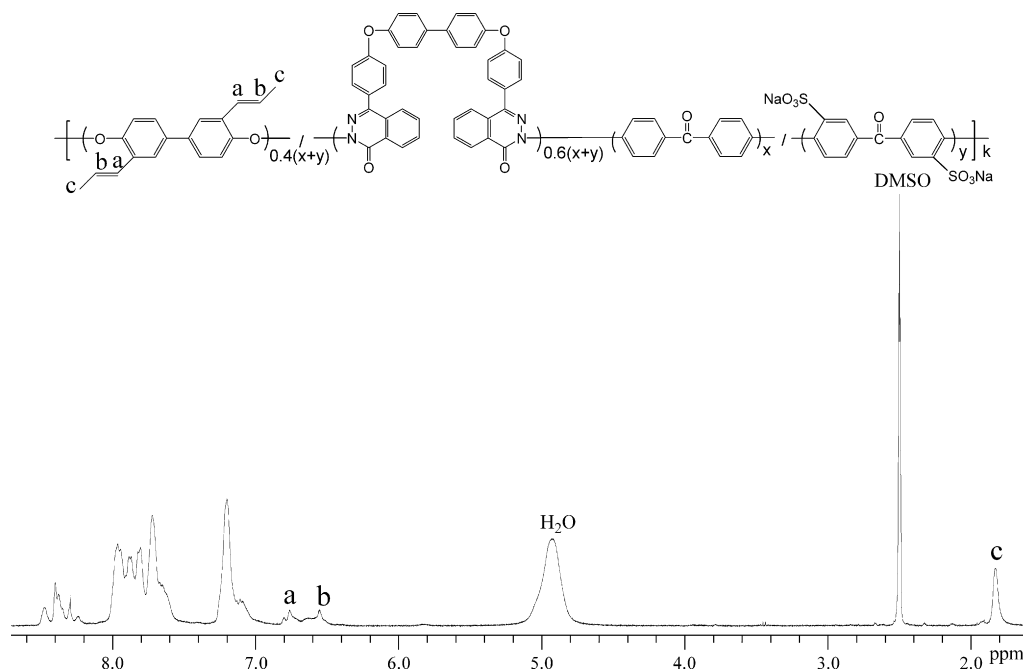


Fig. 1. ¹H NMR spectrum of polymer **6c**.

Table 2
The properties for the virgin polymers and the cross-linked polymers

Sample	Mechanical property		Water uptake (%)	Swelling ratio (%)	Volume swell (%)	Oxidative stability (h:min)	Proton conductivity ($\times 10^{-3}$ S cm $^{-1}$)	Gel content (wt%)
	Tensile strength (MPa)	Elongation at break (%)						
6a	75.05	30.19	1.6	0.5	1.1	3:20	0.056	–
6b	44.83	32.49	8.5	2.5	6.8	2:30	3.345	–
6c	42.71	24.03	18.5	6.2	22.3	1:40	4.318	–
6d	49.82	16.31	52.9	15.5	60.2	1:20	8.263	–
6e	36.69	4.38	136.5	56.8	270.5	0:30	11.077	–
6a^c	106.1	5.58	0.9	0.2	0.6	4:10	0.020	97
6b^c	62.25	10.68	6.5	2.5	6.0	2:50	0.957	91
6c^c	60.53	10.39	14.5	4.2	12.1	2:20	3.514	94
6d^c	67.38	8.37	36.5	9.8	35.6	1:40	5.879	84
6e^c	58.24	3.26	50.6	42.6	160.8	0:50	9.675	76
Nafion 117	21.88	202.5	30.6	21.8	75.4	^a	20.07	–

^c denotes the crossed-SPAEs.

^a After 5 h, it is undegradable.

with Fig. 1, we can see that the allyl group of the 3,3'-diallyl-4,4'-dihydroxybiphenyl was changed to propenyl group in the process of the polymerization at the temperature above 160 °C. This is because that the potassium carbonate in the reaction mixture acted as the base-catalyze of isomerization of allyl group to propenyl group [41,42]. This structure is more stable and similar to that of styrene, it is easier to be initiated and form cross structure.

The oxidative stability to peroxide radical attack was investigated by measuring the elapsed times that a membrane began to break after immersion of each sample into Fenton's reagent (3 wt% H₂O₂ + 2 ppm FeSO₄) at 80 °C. The result is listed in Table 2. It is evident that the oxidative stabilities decreased with increasing S.D. value and the membranes of cross-linked SPAEs exhibited more oxidative stability than those of the virgin SPAEs. This is because that the water uptake increases with increasing S.D. value, and the higher water uptake provides more opportunities for the peroxide radical to attack the polymers. The cross-linking decreased the water uptake and the cross-linked linkages improved the stability of the SPAEs, so the cross-linked SPAEs showed more oxidative stability. As to Nafion, its main chain is full of C–F linkages and F is the strong electron withdrawing group, which has more oxidative stability than the C–H linkages of the main chain of the SPAEs. The cross-linked SPAEs have more oxidative stability than the reported SPAEs under same conditions in case the IEC is same [13,39].

Thermal stabilities of the SPAEs were investigated by both TGA and DSC technologies. Specimens were heated to 150 °C and held at this temperature for 20 min to remove absorbed moisture. They were then cooled to 70 °C and heated again to 600 °C at 20 °C min⁻¹. The TGA curves of both virgin SPAEs **6a–e** and cross-linked polymers **6a^c–e^c** are shown in Figs. 2 and 3, respectively. It is evident that two series TGA curves show similar changing trend, indicating that the cross-linked linkages on the backbone also decomposed at the same temperature of the first-step decomposition or the virgin samples were cross-linked above 250 °C. A two-step degradation profile of the polymers was observed as can be seen in Figs. 2 and 3. The first step

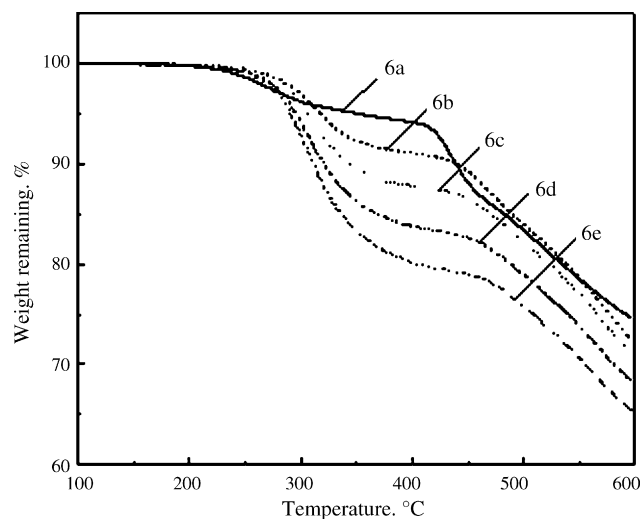


Fig. 2. TGA curves of sulfonate poly(phthalazinone ether ketone)s **6a–e**.

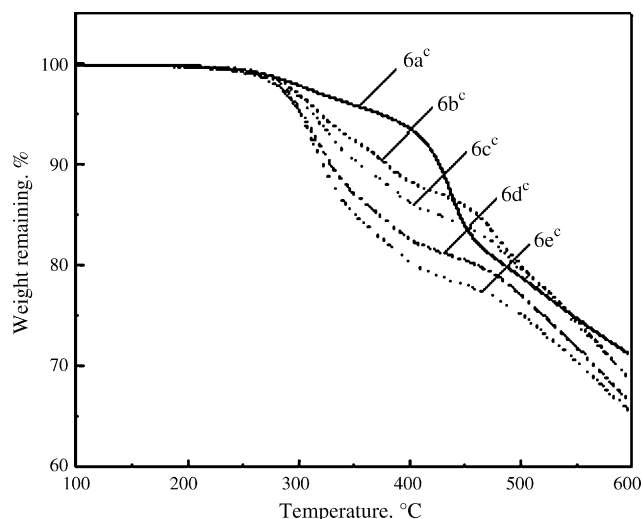


Fig. 3. TGA curves of the cross-linked sulfonate poly(phthalazinone ether ketone)s **6a^c–e^c**.

occurred at around 250 °C and the second thermal degradation took place at about 450 °C. The degradation of the first step was assigned to the sulfonic acid group decomposition, while the second weight loss peak was due to main-chain degradation. It can be seen from Fig. 2 that the percentage of the first weight loss increased with the increase of sulfonation degree. From DSC curves of the polymers, there was no glass transition temperature observed in the range of 50–250 °C before thermal decomposition. This is the inherent nature of highly sulfonated polymers or ionomer nature. The T_g of these polymers are higher than the first decomposition temperature. The increase in T_g is believed to result from the intermolecular reactions of sulfonic acid groups.

4.4. Mechanical properties of the cross-linked SPAEs

The mechanical properties of the membranes **6a–e** and **6a^c–e^c** are summarized in Table 2. The tensile strength of the virgin SPAEs **6a–e** was smaller than that of the cross-linked ones **6a^c–e^c**, while the elongation at break of the original SPAEs was greater than that of the cross-linked polymers. Concerning the inherent viscosity (molecular weight), both tensile strength and the elongation at the break decreased with increasing sulfonic acid group content. This is because the presence of sulfonic acid groups on backbone can decrease the covalent nature while increase the ionic nature of the sulfonated polymer. Because the proton conductivity increases with the increasing sulfonic acid group content, the mechanical property decrease with increase of the proton conductivity. It can be also seen that the tensile strength of the membrane can be enhanced greatly by the cross-linking reaction in the dry state. It is believed that the wet strength of these membranes should exhibit much high value when compared with the virgin polymers. It further proved that the virgin polymers had been cross-linked by comparing the mechanical properties between the virgin polymers and the cross-linked polymers. The tensile strengths of these SPAEs were higher than Nafion 117s, and the elongation at the break was lower than Nafion 117s.

The swelling ratio and the volume swell of the membranes were measured at 80 °C in water for 24 h (Table 2). As expected, the swelling ratio and the volume swell of the membranes increased with the sulfonation degree, IEC and the water uptake increasing. This is because that the sulfonic acid groups are hydrophilic and the presence of sulfonic acid groups on backbone can decrease the covalent nature while increase the ionic nature of the sulfonated polymer. The cross-linking linkages increased the interaction of the polymers and the cross-linking restrained the swell volume to hold water, therefore, the cross-linked membranes showed smaller volume swell degree than virgin membranes. The cross-linking methodology can effectively improve the dimensional stability of the sulfonated polymer membranes.

4.5. Water uptake and proton conductivity

The water uptake and proton conductivity of the synthesized polymer membrane are tabulated in Table 2. The water content

and water state in the sulfonated polymers are very important factors that directly affect proton transport across the membranes [43–45]. Generally, it is believed that protons can be transported along with hydrogen-bonded ionic channels and cationic mixtures such as H_3O^+ , $H_5O_2^+$, and $H_9O_4^+$ in the water medium. In a fully hydrated state, sulfonated polymers may dissociate immobile sulfonic acid groups and mobile protons in aqueous solution. Accordingly, the proper water content level should be maintained in sulfonated polymer membranes in order to guarantee high proton conductivity. These membranes show that water uptake were strongly dependent upon the content of sulfonic acid groups and also related to IEC values. However, it is known that when the content of protonic acid group to be introduced increases, hydrophilicity and water absorption of the sulfonated polymer increase, resulting in the increase of water-soluble and dimensional unstable nature. It can be also seen that from Table 2 the cross-linking can constrain the water uptake to a limited level and almost do not affect the proton conductivity. As to Nafion 117, it has more water uptake and proton conductivity than the SPAEs when the IEC of the Nafion and the SPAEs is equal, which is due to the more polar character of the sulfonic acid function of Nafion 117 and the different microstructural features between the Nafion 117 and the SPAEs that the water filled channels in SPAEs are narrower compared to those in Nafion [46,47]. The polymer **6d^c** and **6e^c** had proton conductivities of 5.9×10^{-3} and $9.7 \times 10^{-3} \text{ S cm}^{-1}$, respectively. The proton conductivity of Nafion 117 under same condition was $20.07 \times 10^{-3} \text{ S cm}^{-1}$. Therefore, **6d^c** and **6e^c** showed potential application in PEM fuel cell, in terms of water uptake, the mechanical property, oxidative stability and proton conductivity.

5. Conclusions

Cross-linked sulfonated poly(arylene ether)s were successfully synthesized by introducing cross-linkable group into sulfonated poly(phthalazinone ether ketone) followed by thermal cross-linking reaction. By cross-linking methodology, the synthesized polymers could fulfill the contradiction of the high sulfonation degree and the dimensional stability. The cross-linked membrane obtained from above polymer had equivalent IEC ($2.27 \times 10^{-3} \text{ mol g}^{-1}$) and proton conductivity ($9.675 \times 10^{-3} \text{ S cm}^{-1}$) when compared to the virgin membranes and Nafion 117 at 25 °C 100% humidity. Moreover, the cross-linked reaction can obviously improve the oxidative stability of the prepared membrane without the loss of proton conductivity.

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